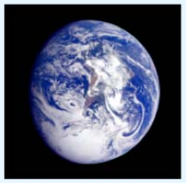
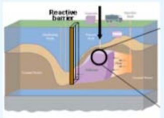
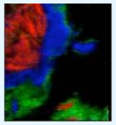
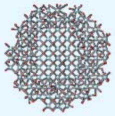
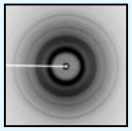
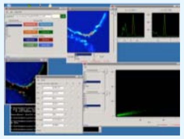




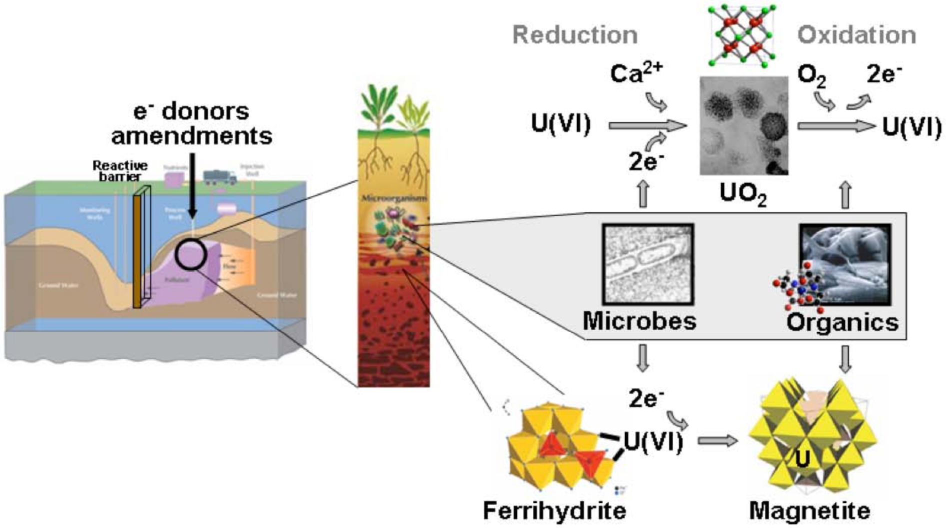






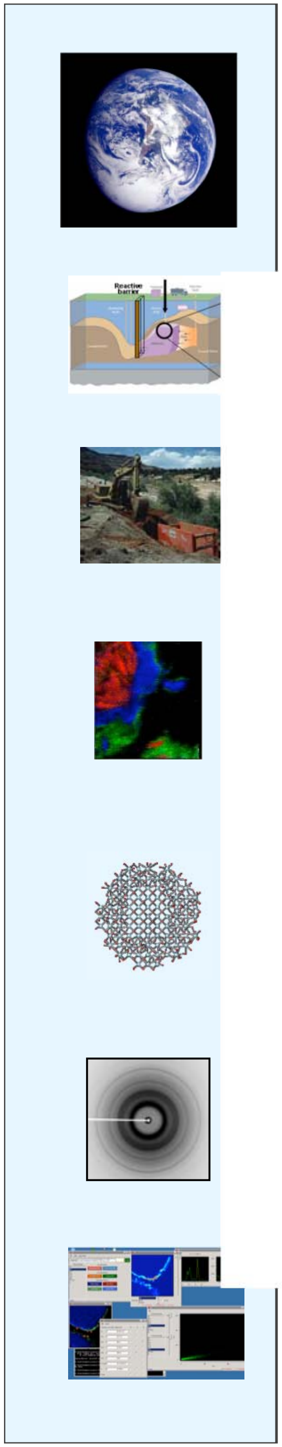


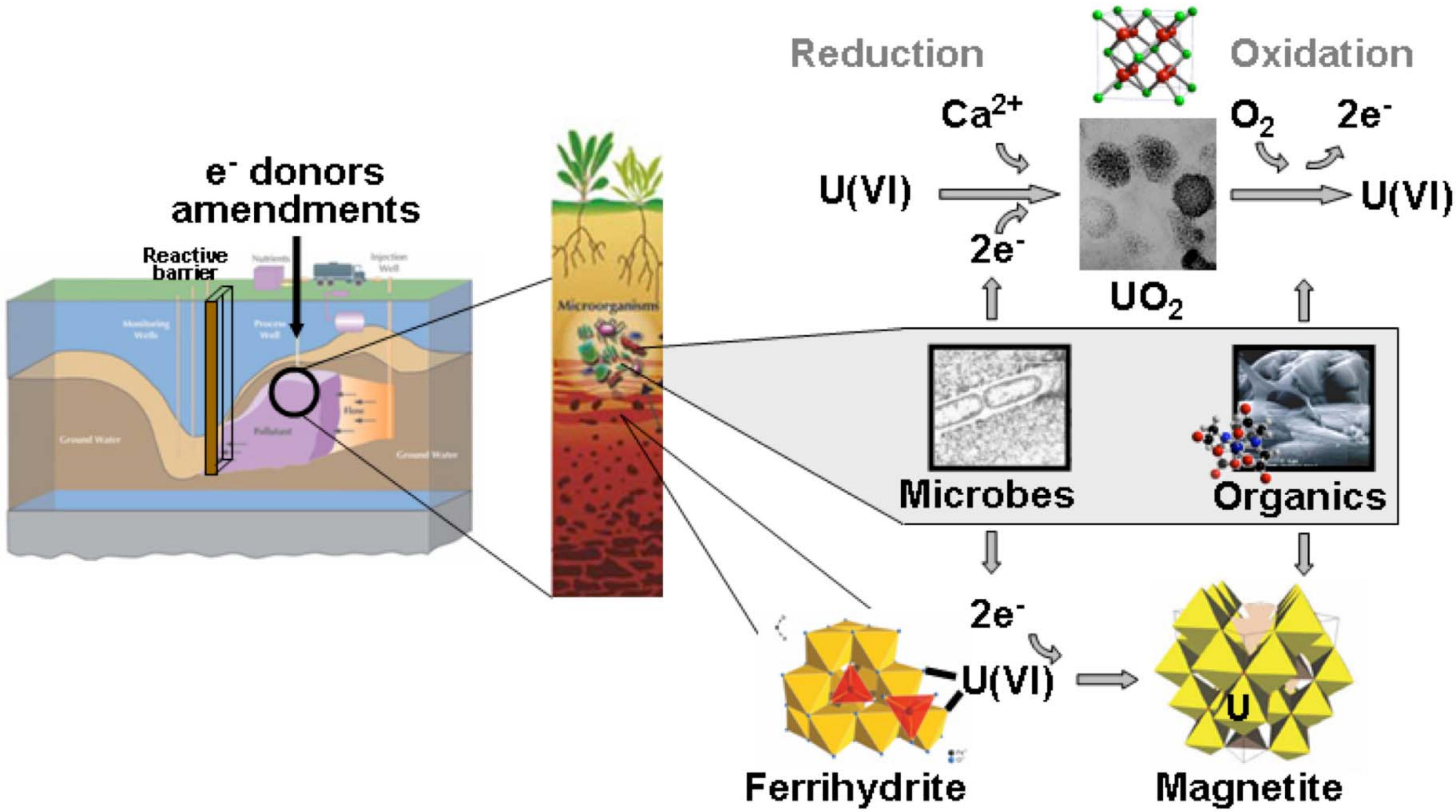
SSRL Environmental Remediation Science Program

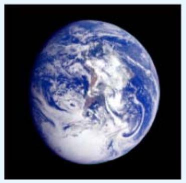
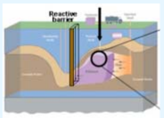


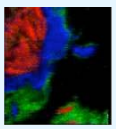
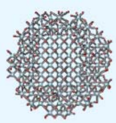
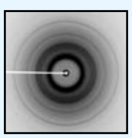
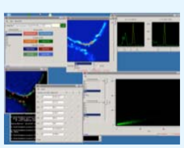
3rd Annual DOE-ERSP PI Meeting
Lansdowne, VA, April 9, 2008

Molecular-Scale Processes





ERSP Mission Context

The problem…

- 2/3rds of DOE sites have uranium subsurface contamination
- > 1 trillion gallons of contaminated ground water
- Pu contamination problematic at Hanford, LANL, INL, ORNL, NTS

Natural and stimulated bioreduction – *First order questions…*

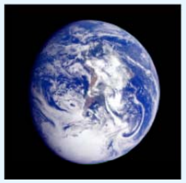
- Thermodynamic identity, properties of biogenic UO_2, PuO_2
- Improve the stability, yield, rate of biogenic UO_2 production

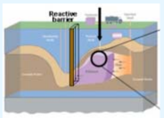
Natural and stimulated attenuation of U, Pu by Fe oxides – *Questions…*

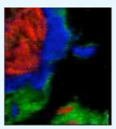
- Structures of natural ferrihydrite, and ion incorporation mechanisms
- Fate of metals during ferrihydrite reductive transformations
- How to stimulate incorporation of contaminants into Fe oxides

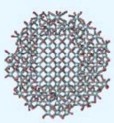
Pathways to site remediation and closure – *First order questions…*

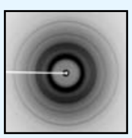
- Characterize site-specific geochemical processes, contaminant speciation
- Optimize, implement, and monitor remediation technologies

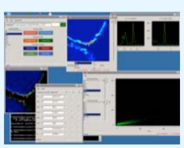






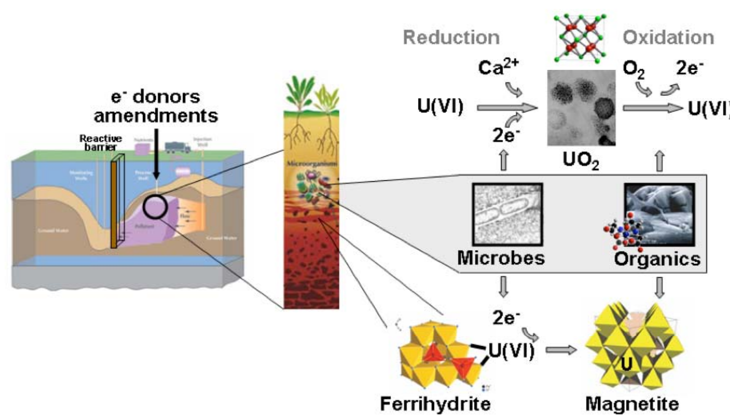


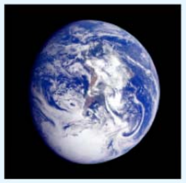


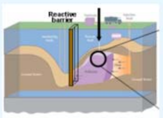


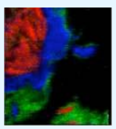
OBJECTIVES: *to contribute enduring knowledge of key biogeochemical processes governing the subsurface behavior of priority contaminants. Emphasis on solid phases and solid-solute interactions.*

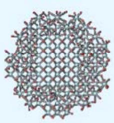
IMPACT: *Enhanced bioremediation of subsurface U and Pu, accelerated clean-up and closure of contaminated sites at savings to US taxpayers, increased public and regulatory acceptance of pathways to closure.*

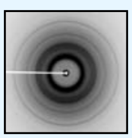


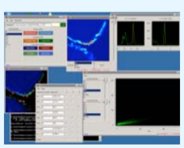












Collaborators

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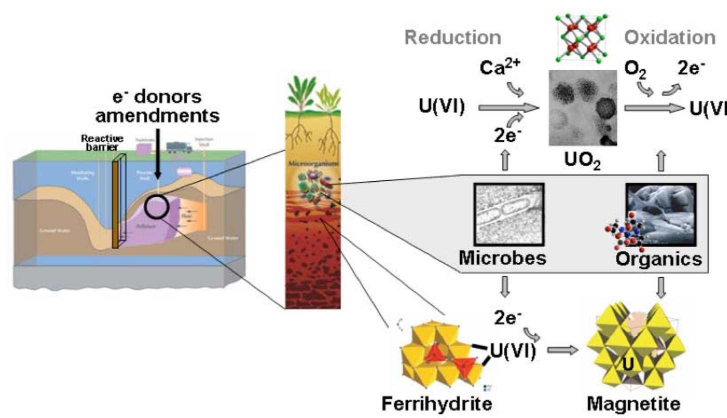
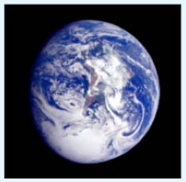
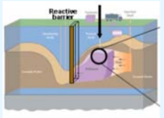
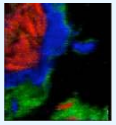
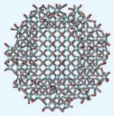
Rizlan Bernier-Latmani (EPFL)
Hakim Boukhalfa (LANL)
Gordon Brown, Jr. (Stanford)
David Clark (LANL)
Jim Davis (USGS)
Peter Eng (U Chicago)
Scott Fendorf (Stanford)
Chris Fuller (USGS)
Dan Giammar (WUStL)
Apurva Mehta (SSRL)
Eric Pierce (PNNL)
Paul Reimus (LANL)
Lynne Soderholm (ANL)
Dawn Wellman (PNNL)
Peter Nico (LBL)
Ken Kemner (ANL)

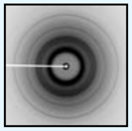


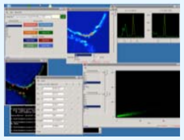






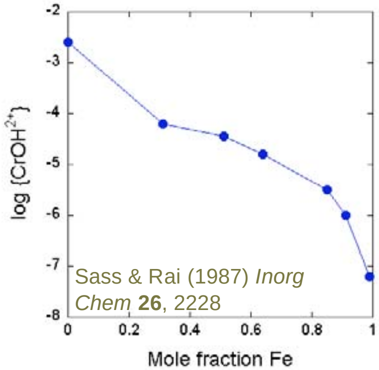






Emphasis: structure ↔ reactivity of complex natural solids

Fe oxides in soils



Fe incorporation & CrOOH solubility

Roles of environmental solids

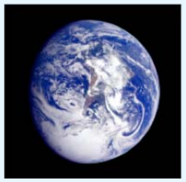
- Sorptive agents
- Contaminant sources
- Oxidants/reductants
- Long-term sinks for contaminant attenuation

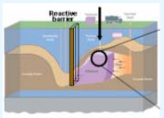
Focus: biogenic UO_2, PuO_2, Fe-oxides

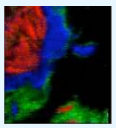
Structure/composition affect reactivity

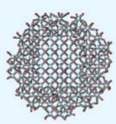
- Structure and composition are variable
  - solid solution of foreign ions can enhance stability
  - lower solubility, oxidation/dissolution rates
  - requires *structural incorporation*
  - aging

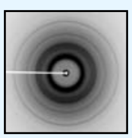
Prediction and manipulation of material properties in the field requires knowledge of structure and composition.

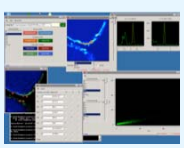












Interfacial structure is important

Biogenic UO_2, PuO_2, ferrihydrite: *nanoparticulate*

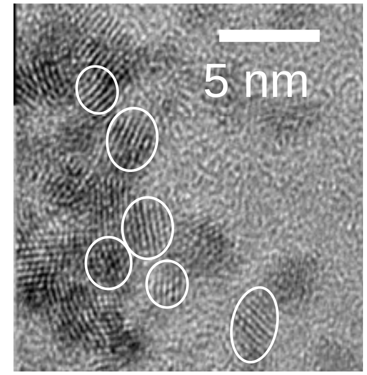
Large fraction of atoms at surfaces

Surface energy can become significant in comparison to bulk energy

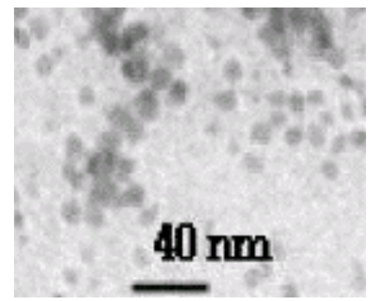
Surface structure mediates:

- adsorption of cations
- incorporation of ions, e.g., U, Ca^{2+} in nanoparticles
- electron transfer mechanisms
- dissolution mechanisms

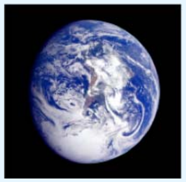
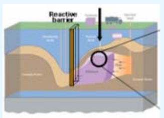
Corrosion occurs at surfaces

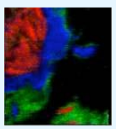
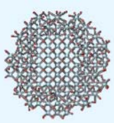
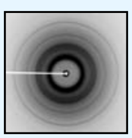
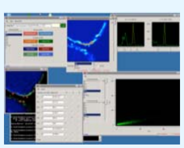


Biogenic UO_2



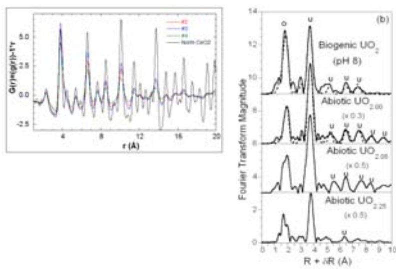
Ferrihydrite

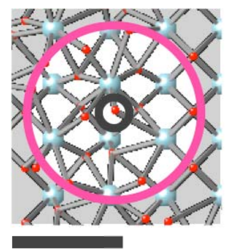
Advanced structure characterization techniques

Local/intermediate range structure: *EXAFS, XPDF*

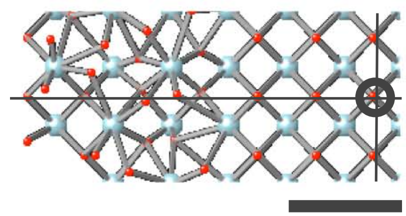


Structural defects

Structural environment around dopants



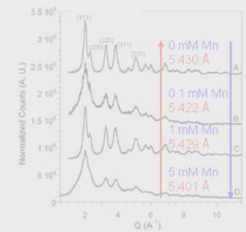
5 Å



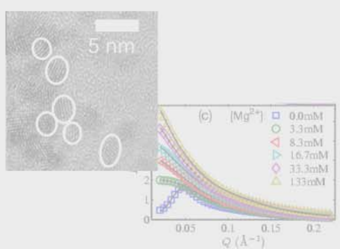
5 Å

Structure at nanoparticle terminations

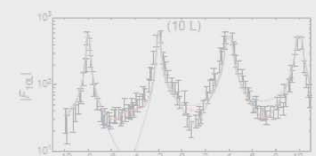
Long-range structure: *SR-PD*



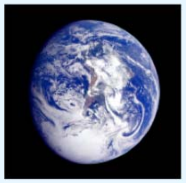
Nano-scale structure: *HR-TEM, SAXS*

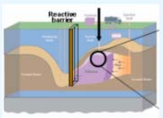


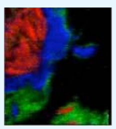
Interfacial structure: *CTR, GI-PD*

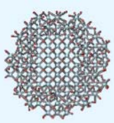


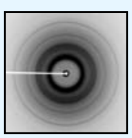
Advanced structure characterization techniques

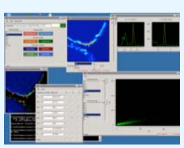




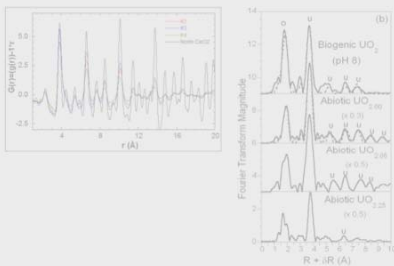




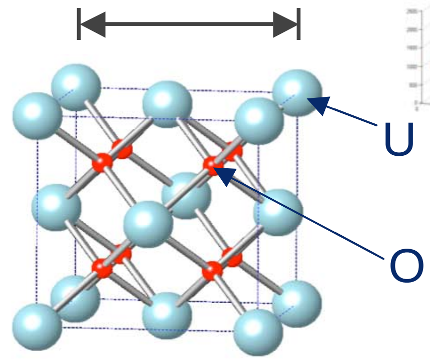




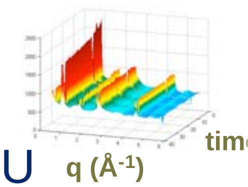
Local/intermediate range structure:
EXAFS, XPDF

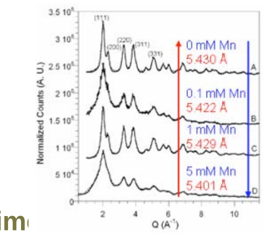


Unit cell dimension



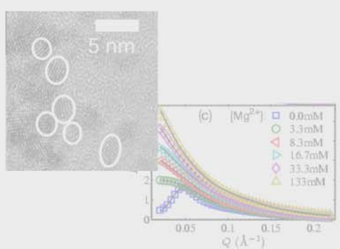
Long-range structure:
SR-PD



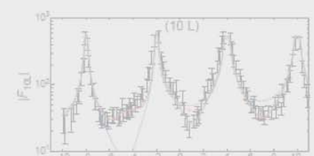


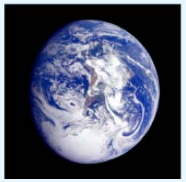
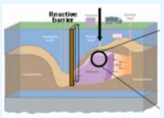
Lattice strain
Foreign ion incorporation
Rates of mineral transformations

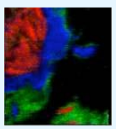
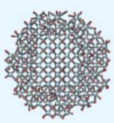
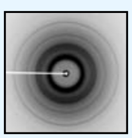
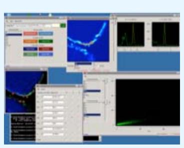
Nano-scale structure:
HR-TEM, SAXS



Interfacial structure:
CTR, GI-PD

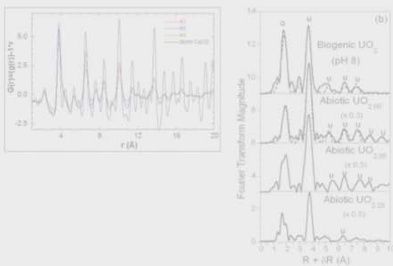


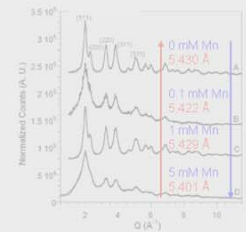





Advanced structure characterization techniques

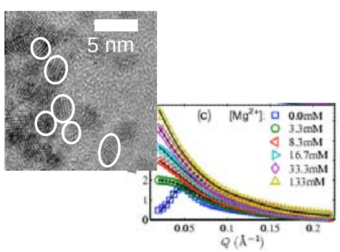
Local/intermediate range structure: *EXAFS, XPDF*

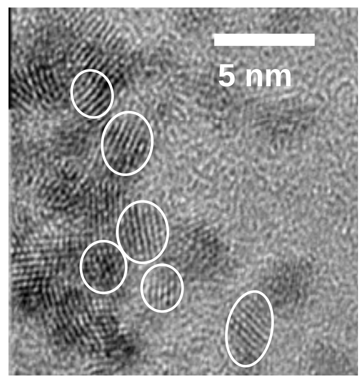


Long-range structure: *SR-PD*



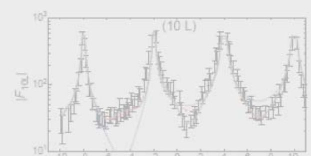
Nano-scale structure: *HR-TEM, SAXS*



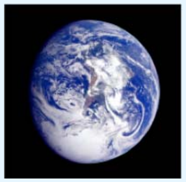


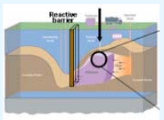
Size, shape, structural defects

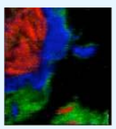
Interfacial structure: *CTR, GI-PD*

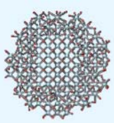


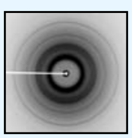
Advanced structure characterization techniques

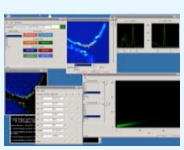




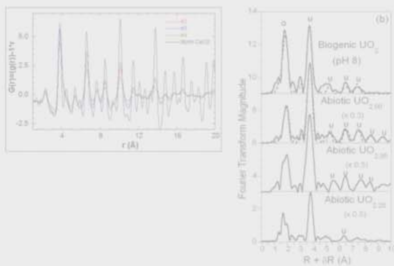




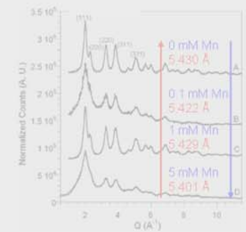


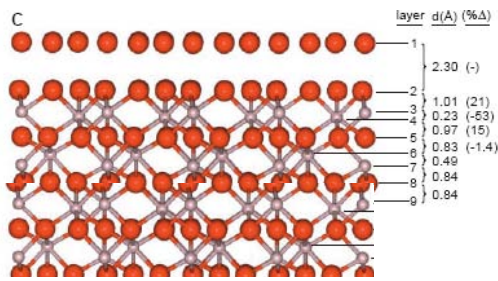


Local/intermediate range structure:
EXAFS, XPDF



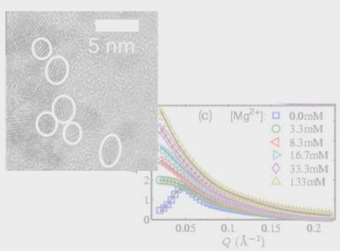
Long-range structure:
SR-PD



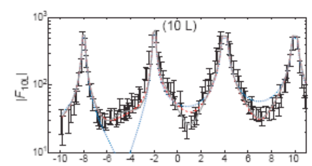


Atom & water positions
Corrosion products

Nano-scale structure:
HR-TEM, SAXS

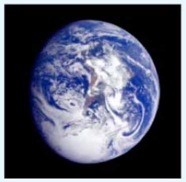
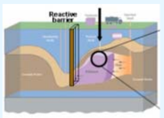


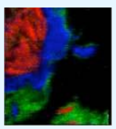
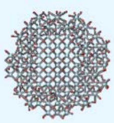
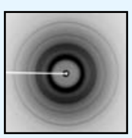
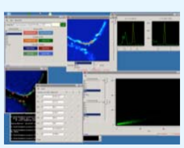
Interfacial structure:
CTR, GI-PD



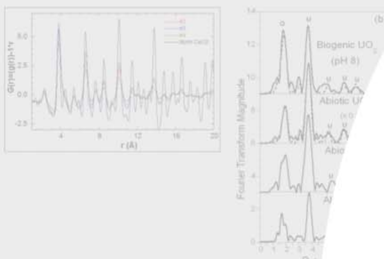
Eng *et al.* (2000) *Science* **288**, 1029

Dramatically clearer picture of structure and sequestration mechanisms

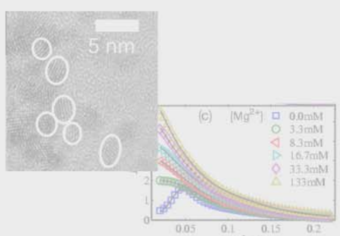



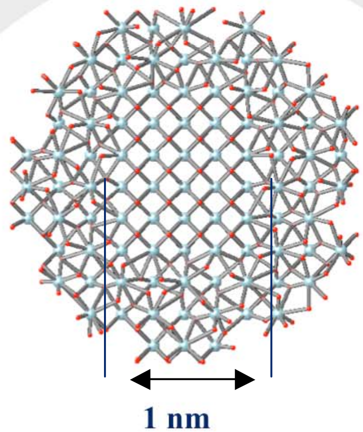





Local/intermediate range structure:
EXAFS, XPDF

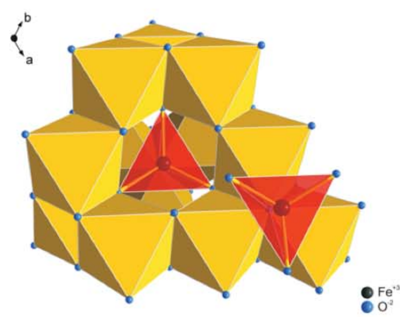


Nano-scale structure:
HR-TEM, SAXS



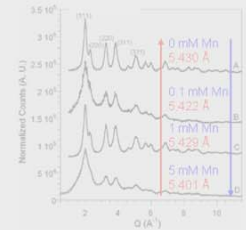


Biogenic UO_2
Schofield *et al.*, in review

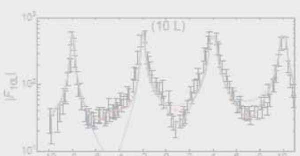


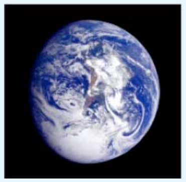
Ferrihydrite
Michel *et al.*, *Science* (2007) **316**, 1726

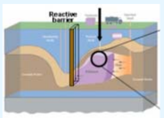
Long-range structure:
SR-PD

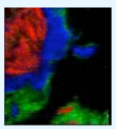


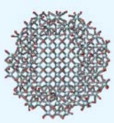
Interfacial structure:
CTR, GI-PD

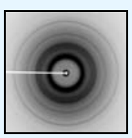


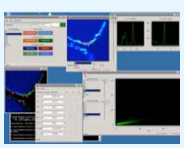






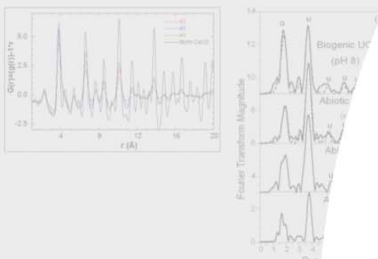




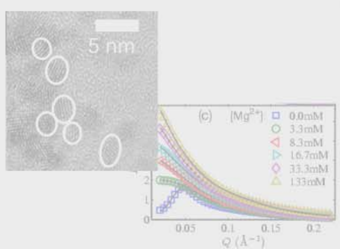


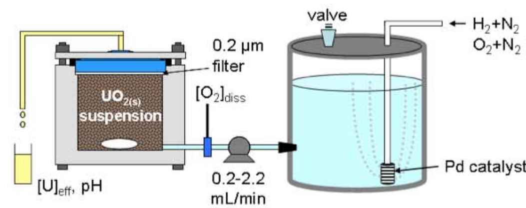
Correlate with reactivity

Local/intermediate range structure:
EXAFS, XPDF



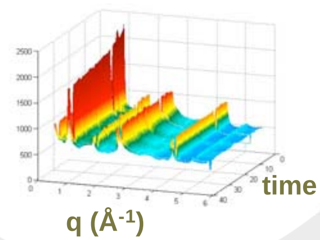
Nano-scale structure:
HR-TEM, SAXS



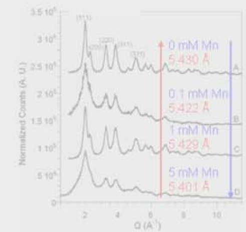


Reactivity:
Solubility
Sorptive capacity
Redox kinetics
Dissolution kinetics
Mineral transformations
Microcosm and columns

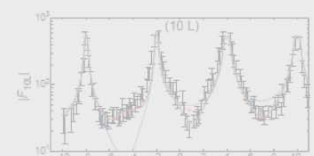
Structure ↔ Property Relationships

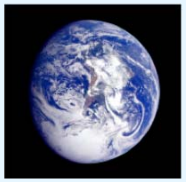


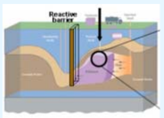
Long-range structure:
SR-PD

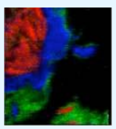


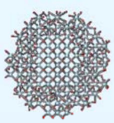
Interfacial structure:
CTR, GI-PD

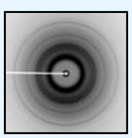


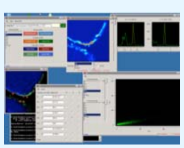












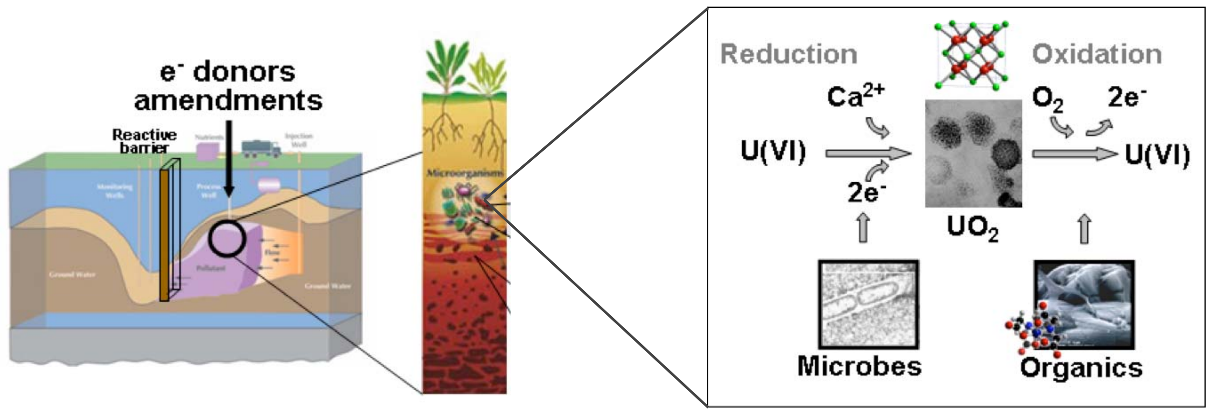
Subtask 1: *Molecular-scale structure, dynamics, and environmental stability of biogenic UO_2*

(Bargar, Bernier-Latmani, Giammar, Clark, Eng, Soderholm)

Hypotheses:

Module 1: How do foreign solutes moderate biogenic UO_2 reactivity?

(I) Incorporation mechanisms of groundwater cations ↔ stability.
(II) Ability of corrosion coatings to passivate/stabilize nanoparticles (Ca^{2+}, SiO_4^{4-}).
(III) Effect on meter-scale behavior of U.

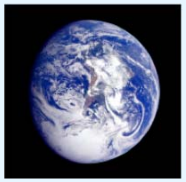
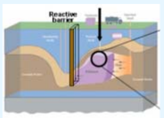


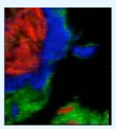
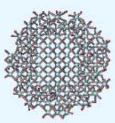
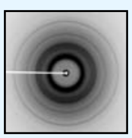
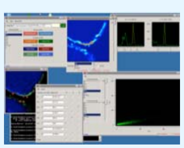
Module 2: Structure/reactivity of UO_2–water interfaces, corrosion coatings.

(I) Molecular-scale structure of UO_2-water interfaces.
(II) Role of hyperstoichiometry on surface reactivity at molecular scale.
(III) Sorption/passivation of UO_2 by Ca^{2+} and SiO_4^{4-}.

Module 3: How do proteins moderate UO_2 nucleation and growth?

(I) Do proteins bind to biogenic UO_2, limiting or arresting crystal growth?
(II) Does protein binding alter susceptibility to re-oxidation?

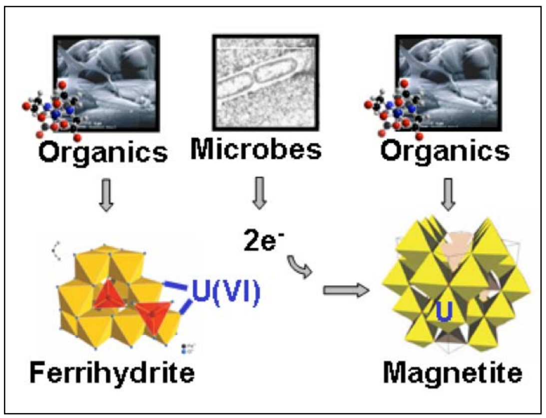
Subtask 2: *Molecular-scale structure, dynamics, and U binding mechanisms of natural Fe oxides*

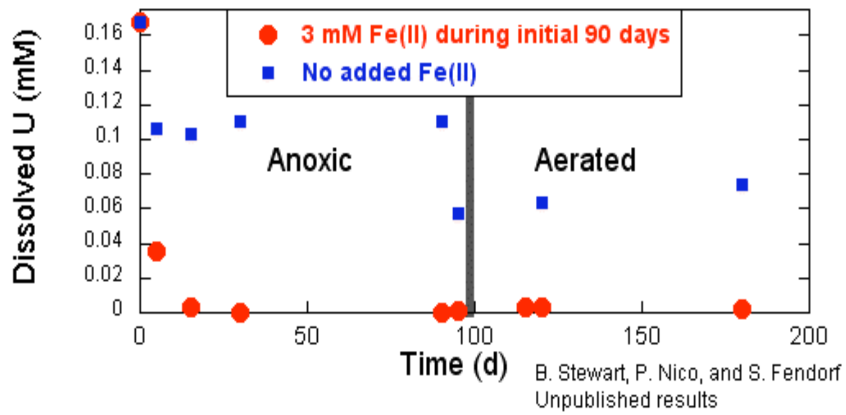
(Brown, Fendorf, Bargar)

Questions and Hypotheses:

Module 1: Ferrihydrite structure and reactivity.

(I) Structure of natural FHY? Incorporation of ions ↔ structure, reactivity?
(II) Role of tetrahedral Fe^{3+}?





Module 2: U attenuation via Fe reduction and ferrihydrite transformation.

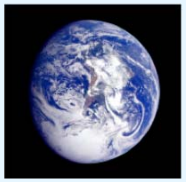
(I) Transformation products, rates, processes.
(II) U incorporation: mechanisms, rate/extent.

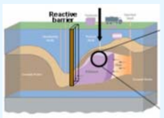
Module 3: Surface reactivity of Fe oxides.

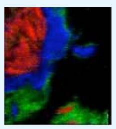
What factors control the relative sorptive capacities of natural Fe oxides?

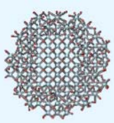
Module 4: Role of microbes and NOM on U sorption and reduction

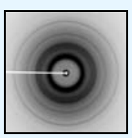
How do biofilms moderate reaction of metal ions with natural Fe oxides?

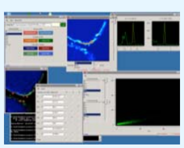






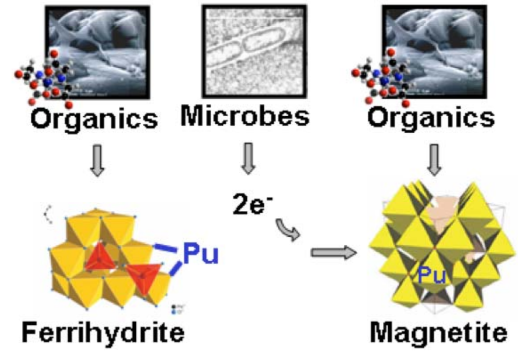






Subtask 3: *Molecular mechanisms of Pu binding by environmental solids*

(Boukhalfa, Bargar)



(I) Structure/reactivity of biogenic PuO_2

(II) Speciation of Pu in Fe oxides during redox cycling

(III) Mechanisms of Pu adsorption on biogenic Mn-, Fe-oxides

Further details will be provided in LANL-SFA talk that follows

Subtask 4: *Site characterization, remediation, and repository performance assessment*

(I) Processes and longevity of permeable reactive barriers for groundwater U remediation at Fry Canyon, Utah (C.C. Fuller, USGS)

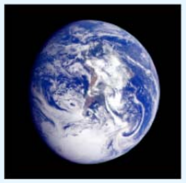
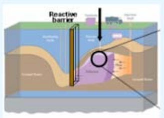
(II) Polyphosphate treatment of the Hanford 300 Area deep vadose and capillary fringe uranium contamination (D. Wellman and E. Pierce, PNNL)

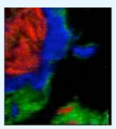
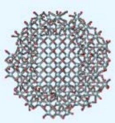
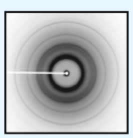
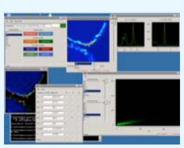
(III) Uranium fate and transport in sediments at Yucca mountain (P. Reimus)

(IV) Uranium transport, dissolution, and desorption processes in the Hanford vadose zone (G. E. Brown, Jr., Stanford University)

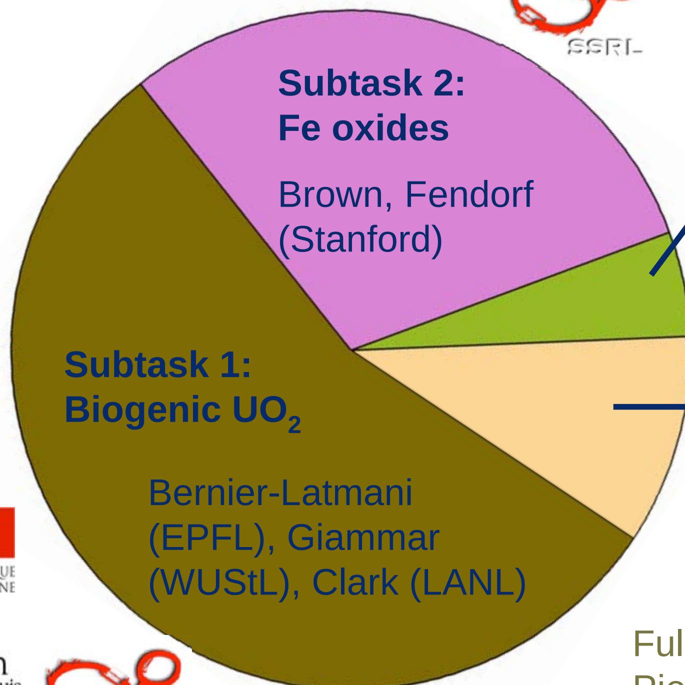
(V) In-situ bioremediation of a uranium-contaminated aquifer at the Rifle site (J.A. Davis, USGS)

New collaborations are anticipated over time.

The Project

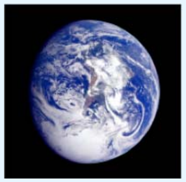


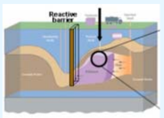
Subtask 3: Pu binding by solids

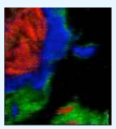
Boukhalfa (LANL)

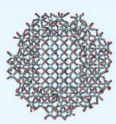
Subtask 4: Site-specific contaminant geochemistry

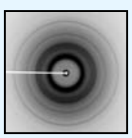
Fuller (USGS), Wellman, Pierce (PNNL), Brown (Stanford), Davis (USGS), Reimus (LANL)

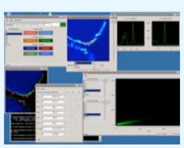










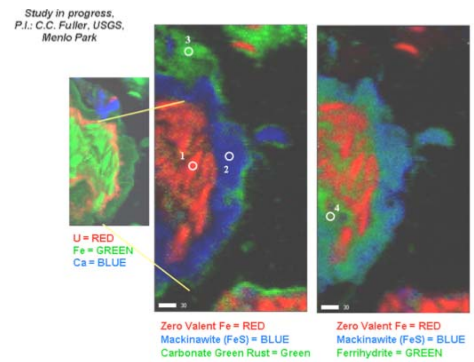


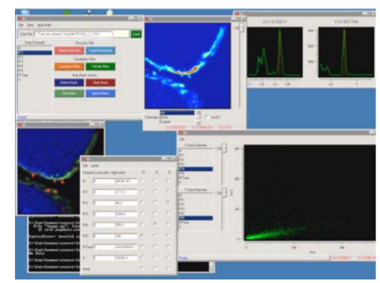
BER-ERSD user support program.

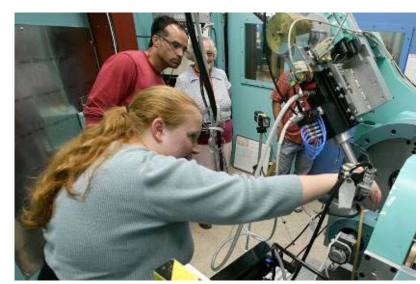
- 7/2004 – 9/2008, Project number 1024605,
- Objectives: facilitate access and utilization of SR-based techniques for BER ERSD-funded and associated research projects.

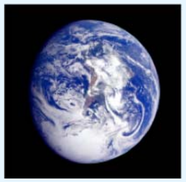
Highlights:

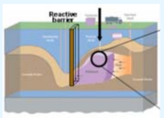
- ERSP research increased by more than 100% each year between FY 05 - 07, indicating success of project.
- 24 ERSD-funded projects, 1,500 8-hour shifts, 36 publications (FY 05-07).
- Supported: XAS, μ-XAS, SR-PD.
- Developed *in-situ* and time-resolved SR-PD capabillity for users
- Designed, implemented, commissioned, and supported a world-class hard x-ray microprobe for ERSD research.
- FY 2007 microprobe ERSD use increased 195% over 06 (first two user years).
- Developed five new data acquisition/ analysis software packages.
- Conducted 4 user education workshops.

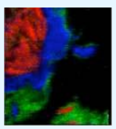


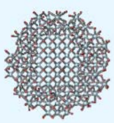


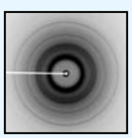


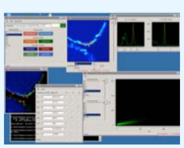










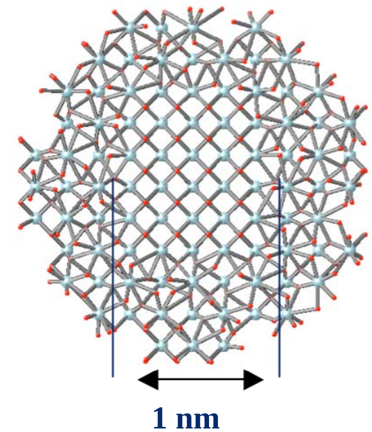


UO_2 structure/reactivity project

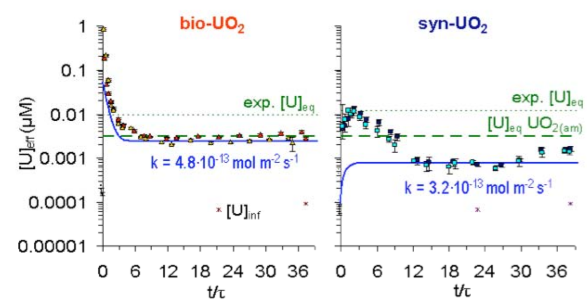
- 4/2006 – 9/2008, Project number 1027869,
- Objectives: characterize the structural chemistry and reactivity of biogenic UO_2, including solubility, dissolution kinetics, and catalytic oxidation by biogenic Mn(IV) oxides.

Highlights:

- Biogenic UO_2 found to be stoichiometric UO_2 and to be *unstrained*, suggesting that interfacial free energy is relatively small. Particles were found to have a highly ordered core of *ca* 1 nm diam, surrounded by a locally contracted outer zone.
- Solubility *similar to that of bulk synthetic stoichiometric* $UO_{2.00}$ (reducing conditions).
- Carbonate increases dissolution rate even at anoxic conditions.
- Mn oxidizing bacteria catalytically accelerate bio-UO_2 oxidation.
- Mn^{2+} is structurally incorporated, increases stability against oxidation.
- Lays the foundation for the proposed project

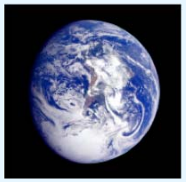


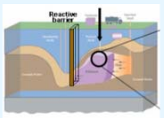
Structure of biogenic UO_2.

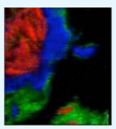


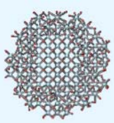
Dissolution of biogenic UO_2 under reducing conditions, pH 7.

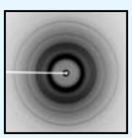
Molecular-scale ↔ remediation & closure

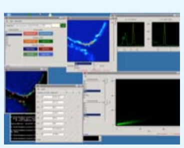




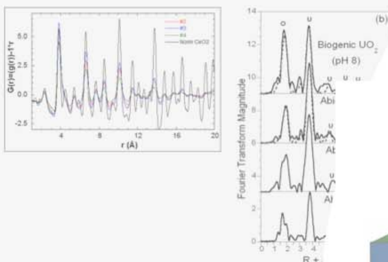




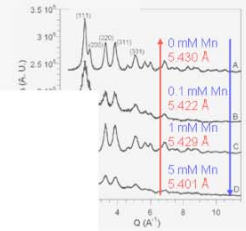


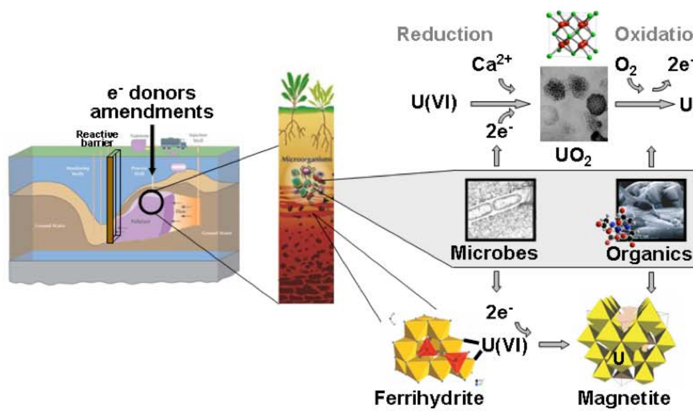


Local/intermediate range structure:
EXAFS, XPDF

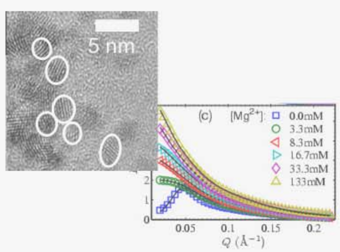


Long-range structure:
SR-PD





Nano-scale structure:
HR-TEM, SAXS



facial
ture:
CTR, GI-PD